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# Polymer Based Nanodielectric Composites

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## 1. Introduction

The rapid expansion of renewable energy applications demands higher efficiency and higher density energy storage and energy conversion systems (Arico et al 2005, Nourai et al 2005). Various DC-AC, AC-AC conversions are needed for solar and wind farms, while primary and secondary electrochemical devices are needed for transportation and telecommunication applications. In addition, military equipment and transport have been actively moving toward more electric systems. High energy density, power density and high temperature components are desired for applications such as active armor, electrochemical guns, directed energy weapons, more electric aircraft, electric launch platform, all electric warships, and so on (Sarjeant 1998, DARPA 2004). Passive components such as capacitors have been a limiting factor in full implementation of high energy density electrical systems. Figure 1 shows the development history of capacitor technology. Every generation of capacitors are primarily credited to the innovation and engineering of new dielectric materials. The advances of such a passive component and active components have provided great foundation for future power electronics and electric power.

Dielectric materials are categorized into organic polymers, inorganic ceramics, filled and unfilled polymeric thin films, ceramic films and nanodielectric composites. Polymer dielectric films show very high dielectric strength ( $>300\text{kV/mm}$ ), lower dielectric loss ( $<0.01$ ), and adequate mechanical flexibility. Single-phase polymers eliminate complexities arising from mixing and dispersion that are prevalent in the multi-phase systems, but, they are subject to low dielectric permittivity or constant ( $<4$ ) and working temperature ( $<200^\circ\text{C}$ ). Ceramic dielectrics tend to have very high dielectric permittivity ( $>100$ ) but relatively low dielectric strength ( $<50\text{kV/mm}$ ). Increasing their dielectric strength is one of the challenges and goals in modern day dielectrics research. The presence of grain boundaries, porosity, impurities, surface defects, and chemical deterioration causes ceramic dielectrics to fail at relatively low field stresses ( $<10\text{kV/mm}$ ). In addition, many ceramic dielectrics have high dissipation factor ( $>0.01$ ), high capacitance loss ( $>30\%$ ) under high voltage stress ( $>3\text{kV/mm}$ ) and/or piezoelectric effect associated with the ferroelectric type ceramics. Thin film dielectrics are an important area leveraging either polymer or ceramic materials. The thin films are usually in nanometer to submicron in thickness with very high breakdown strength. But, they are primarily useful for low voltage and small size microelectronic application. Scalability, reliability, cost and power level are great concerns.

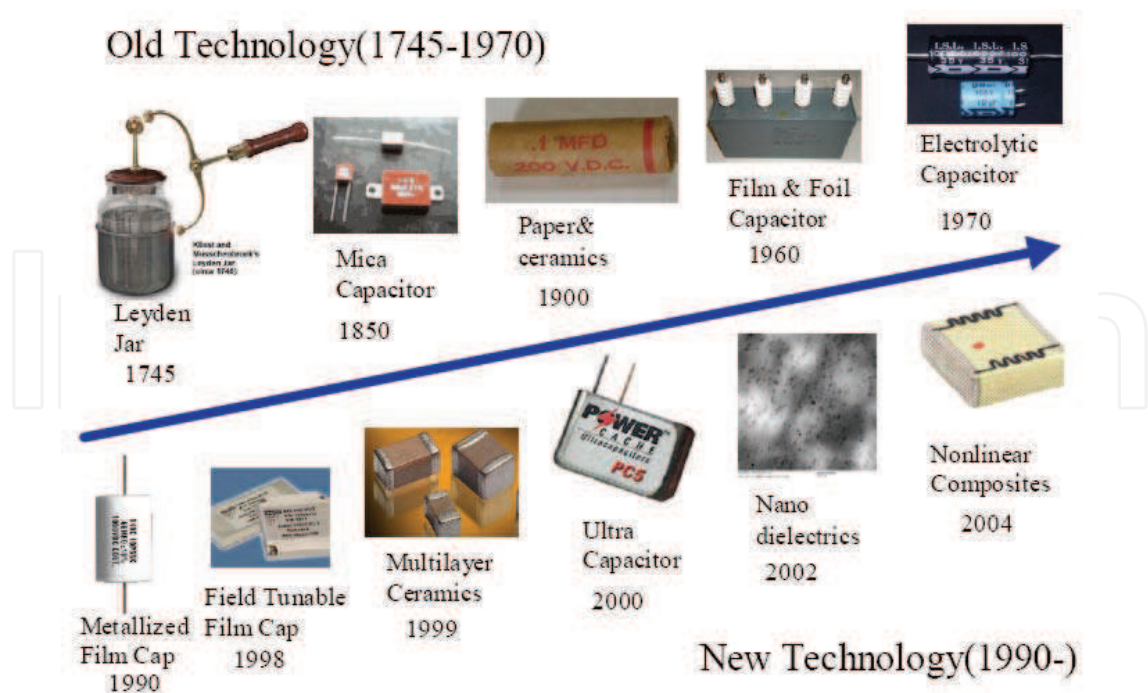


Fig. 1. Evolution of capacitor technology has a close relationship with materials development (Tan et al 2006).

Nanodielectric composites belong to a new type of materials engineered for improved functions, performance for dielectrics and electrical insulation (Lewis 19994). Certain ceramic materials can be selected to blend with polymers to provide synergy between the high breakdown strength polymer and high permittivity ceramic materials as shown in Figure 2. A number of research areas are being actively pursued to fully explore the advantages of the functional composites.

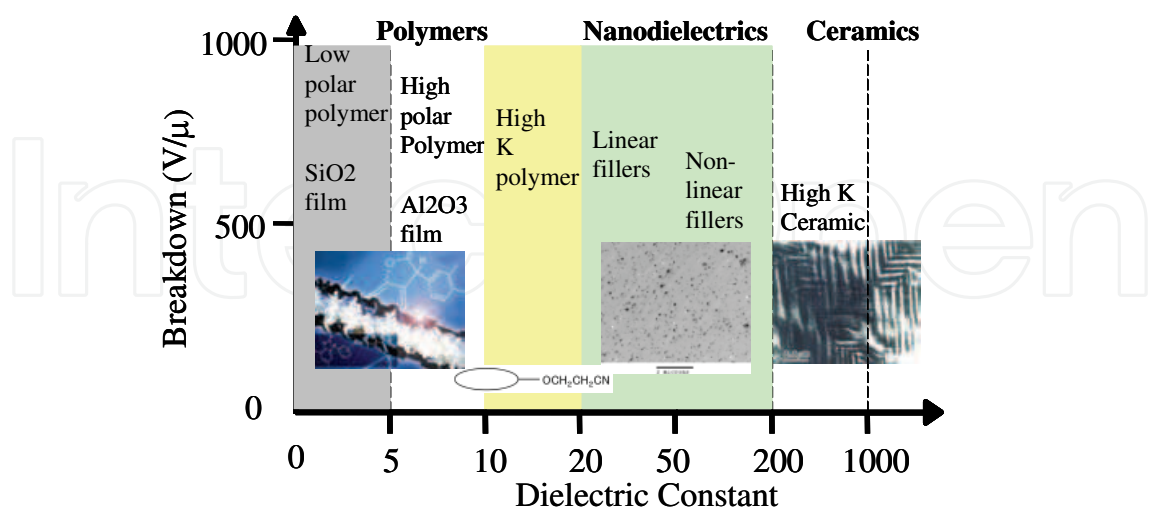


Fig. 2. Relationship between breakdown strength and dielectric permittivity of various dielectric materials (Tan et al 2010).

With properly selected nanoceramic fillers, dielectric properties of the polymers can be improved due to the absence of grain boundaries in ceramics. The chapter will review

existing high performance polymer dielectrics and current nanodielectric engineering efforts. The effect of nanofiller type and size, distribution, particle-polymer interface and the host polymers will be discussed. A better understanding of the issues and fundamental mechanisms in nanodielectric engineering will lead to the successful development and implementation of high performance nanodielectrics.

## 2. High performance dielectric materials

An insulator is a material that resists the flow of electrons due to a full valence band and a large band gap between the valence band and the next higher state. A dielectric material is an electrical insulator that can be polarized by an applied electric field. The internal electric charges only slightly shift from their average equilibrium position resulting in dielectric polarization. Ceramics and polymer-based dielectrics are the most common materials of industrial interests, where the control of the storage and dissipation of electric and magnetic energy in these materials are of great interest. The following section discusses high performance dielectric materials with a focus on high temperature and high energy density capability.

### 2.1 High temperature dielectric materials

Generally speaking, voltage stress, complex dielectric permittivity, breakdown strength, mechanical strength, thermal stability and conductivity are the primary interests for dielectric materials. In many cases, these properties are mutually dependent. For example, the rise in temperature in the core of the capacitor causes an increase in dielectric losses and partial discharge, which can lead to premature failure. Often the self-generated internal heat can overshadow the ambient temperature, which then can lead to a more rapid degeneration and earlier failure. To meet the needs of high temperature devices and equipment, a number of high temperature ceramics and polymer dielectrics have received intensive investigations. This includes Polycarbonate (PC), Polyphenylene sulfide (PPS), Fluorene Polyester (FPE), Diamond like carbon (DLC), polyetherimide (PEI), Polyetheretherketone (PEEK), Polyimide (Kapton® PI), Polytetrafluoroethylene (Teflon®), AlN, AlON, TiO<sub>2</sub>, etc. For applications at or above 200°C, very limited choice of polymers and ceramic materials are available. Table 1. shows a number of high performance polymer and thin film dielectric materials being of interest for capacitor applications (Tan et al 2005). High temperature polymer films such as fluoropolyester (FPE), polyetherimide (PEI), and polytetrafluoroethylene (PTFE) not only meet the 200°C temperature requirement, but also have potential to be further engineered for higher performance. While stable to 260°C, PTFE has poor mechanical stability, difficulty in metallization and lower breakdown strength (<400kV/mm). FPE films are restricted to low energy density due to low permittivity. PEI has been successfully melt extruded into 5μm film. A great combination of dielectric, thermal and mechanical properties offers a good polymer matrix for inorganic fillers.

Ceramic dielectrics are very good high temperature dielectric materials by nature. They can be categorized into linear and nonlinear dielectrics by polarization mechanism as shown in Figure 3. Linear dielectric ceramics have lower dielectric permittivity and relatively higher breakdown strength than nonlinear material. The nanostructured TiO<sub>2</sub> is one example of the category, which has received intensive investigations due to the high energy density projection for capacitor applications [Chao et al 2010].

Properties	BOPP	PVDF	PC*	PPS*	PEEK*	Siloxane	PEI	PTFE	FPE	Kapton™ Polyimide	DLC	ALN
Temp. Range (°C)	90	125	130	150	150	>150	200	260	275	300	350	400
Dielectric Constant	2.2	10	30	3.1	3.2	8.6	3.2	2.1	3.3	3.3	3.3	9
Loss at 1kHz (10 <sup>-3</sup> ) (25 °C)	0.2	15	1.3	0.5	4	60	2	0.5	2.6	2	4	5
Dielectric strength (V/μm)	700	400	350	400	430	380	650	296	520	420	800	>500
Tensile strength (ksi)	4.9	7.5	9.5	36	17.4	N/A	14	3	9.5	10.5	N/A	N/A
Film energy density (J/cc)	4.7	7.1	1.6	2.2	2.6	7.5	6	1.6	3.9	2.5	9.3	9.9
Film process	Extru- sion or blow	Extrusion	Solvent cast	Extru- sion	Extrusion	Solvent cast	Extru- sion	Extrusion or blow	Solvent cast	Solvent cast	Ion beam	Sputt- ering

\*Polycarbonate (PC), Polyphenylsulfide (PPS), Polyetheretherketone (PEEK)

Table 1. High temperature dielectric films for capacitor applications (Tan 2010)

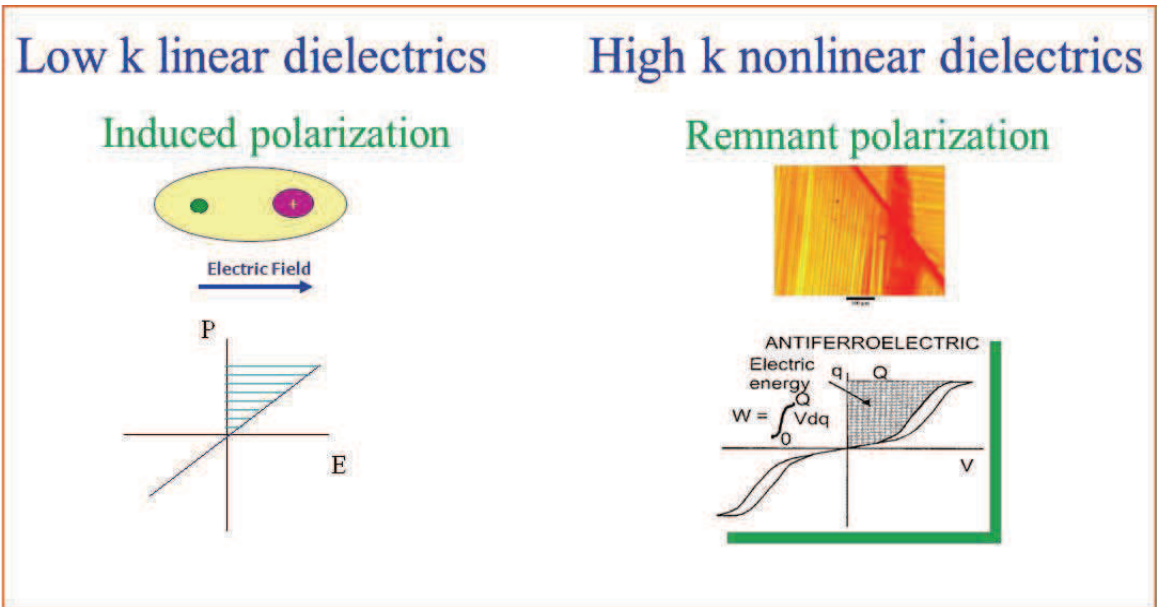


Fig. 3. Dielectric material classifications in terms of their polarization mechanism (Tan et al 2010).

Nonlinear dielectric ceramics exhibit a dipolar orientation mechanism resulting in a very high dielectric constant, but intend to fail easily at relatively low field stresses due to the grain boundary and inherent piezoelectric / electrostrictive effects. Ferroelectric and antiferroelectric materials are representative of this category. Their properties have been exploited by Sandia National Lab and other research labs to fabricate high energy density capacitors for neutron generators and power electronic inverter applications (Tuttle et al 2001, Campbell et al 2002). The hybridization of linear and nonlinear dielectric ceramics was also investigated by TRS Technologies, The Pennsylvania State University and Naval Research Laboratory (Hackenberger et al 2010, Gorzkowski et al 2007). Glass was added into ferroelectric ceramics to improve sintering behavior and to reach high density, however, the



defects and microstructural control in the process created difficulties in reaching high breakdown strength and energy density.

In thin film dielectric approaches, ceramic films received great interest not only for their high breakdown strength appropriate for capacitor applications, but also their high dielectric permittivity needed for high frequency devices and memory applications. Among them are diamond-like carbon (DLC), aluminum oxynitride (AlON), strontium bismuth tantalate, and barium titanate, which are usually deposited on metal foil, Si wafers, or ceramics (Wu et al 2005, Bray et al 2006, Xu et al 1998, Kaufman et al 2010). The thin film technology is generally subjected to lower dielectric permittivity, low film quality in scale-up processes, processing difficulties and therefore low voltage applications.

## 2.2 High energy density dielectric materials

Energy density of a dielectric material is defined by  $\epsilon_0 \epsilon E^2/2$ , where  $\epsilon_0$  is the permittivity of free space,  $\epsilon$  is the permittivity of the dielectric material, and  $E$  is the breakdown strength of the dielectric material. Either raising breakdown strength or dielectric permittivity will result in the increase of the energy density. A survey of dielectric materials has revealed that the combination of high breakdown strength and permittivity are not commonly found in dielectric materials (Figure 4). There have been two different research approaches to increase energy density so far. Increasing the breakdown strength appears to be emphasized the most because of the square relationship in the above definition. However, a great deal of difficulties has occurred particularly in the scale-up of materials. An increasing trend of effort is to seek high dielectric permittivity materials while maintaining breakdown strength of the dielectrics. This effort also finds similarity in other applications such as transistor gate, non-volatile ferroelectric memory, integral capacitors, and transmission lines.

Figure 5 shows the trend of increasing the dielectric permittivity that has been studied for microelectronics, power electronics and electronic actuation (Tan et al 2006). Some ceramics can have the dielectric permittivity of up to  $10^3$ , but they need better engineering to augment breakdown strength. Some highly preferred polymers also show high dielectric permittivity, high breakdown strength and mechanical flexibility. However, a concern to be addressed is the increased dielectric loss. GE has developed some polymer dielectrics that have good combination of dielectric properties and self-clearing capability, which can extend the film life at voltages near the breakdown field of the films.

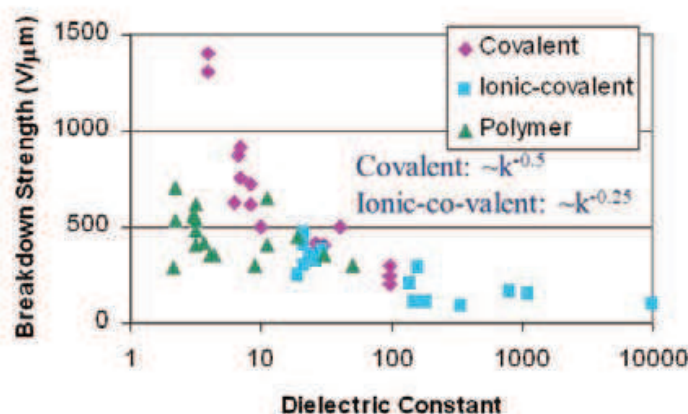


Fig. 4. A survey of dielectric materials with dielectric properties (Tan et al 2010).

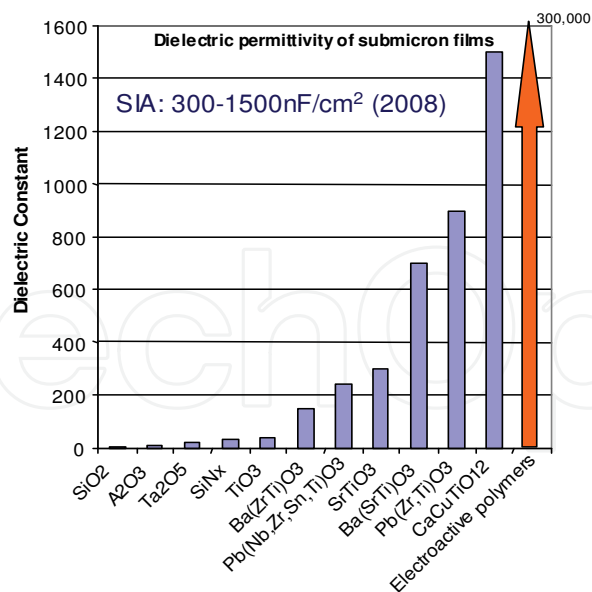


Fig. 5. Dielectrics of interests to microelectronics and electrical systems (Tan et al 2010).

Recently, various governmental agencies have been actively seeking dielectric materials that can offer a high energy density ( $>20\text{J}/\text{cm}^3$ ) and high temperatures ( $200^\circ\text{C}$ ) for pulsed power and power conditioning applications. Figure 6 shows a theoretical design rule for dielectric films to meet a  $25\text{ J}/\text{cm}^3$  energy density requirement. If a dielectric material can have a dielectric permittivity of 10-20, a film with reasonable breakdown strength and thickness can be the great candidate for the purpose. If using a ceramic material with a permittivity of higher than 60, much lower breakdown strength is required. The film in need can be more than  $10\mu\text{m}$  in thickness. Currently, many institutions are actively investigating on dielectric films. The high performance dielectric materials have become one of the strategic thrust in material technology.

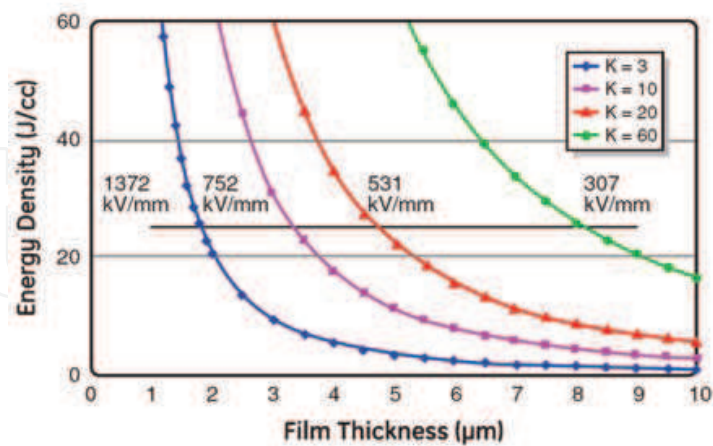


Fig. 6. Relationship of energy density, film thickness, dielectric constant and breakdown strength (Tan 2010).

2.3 Synergistic effect of nanodielectric composites

Polymer based nanodielectric materials have been investigated over the last 10 years for high energy density capacitors and higher corona resistant electrical insulation (Aulagner 1995).

Various investigators have pointed to the challenges of increasing breakdown strength. For example, a homogeneous dispersion of ferroelectric  $\text{BaTiO}_3$  particles were prepared in polypropylene with an in-situ polymerization process (Guo et al 2007). Although the permittivity was increased by almost 3x over polypropylene, the breakdown strength was decreased. The breakdown mechanism was found very complicated particularly for the multi-phase systems. The mismatch of different phases and the various non-uniformity and defects introduced from processing were of critical consideration.

Depending on the filler-matrix interface, the size and shape, and agglomeration of fillers, the charge carriers are facing a more complicated environment under an electric field. Figure 7 shows a typical nanoparticle distribution in a Ultem™ polyetherimide (PEI). Agglomeration and aggregation are a great issue for the dry particles (left). Better particle dispersion could be achieved if solution prepared nanoparticles (right) are used, however, many desired materials are not available in solution or in large quantity. This would be an area of interest that need more in-depth investigations.

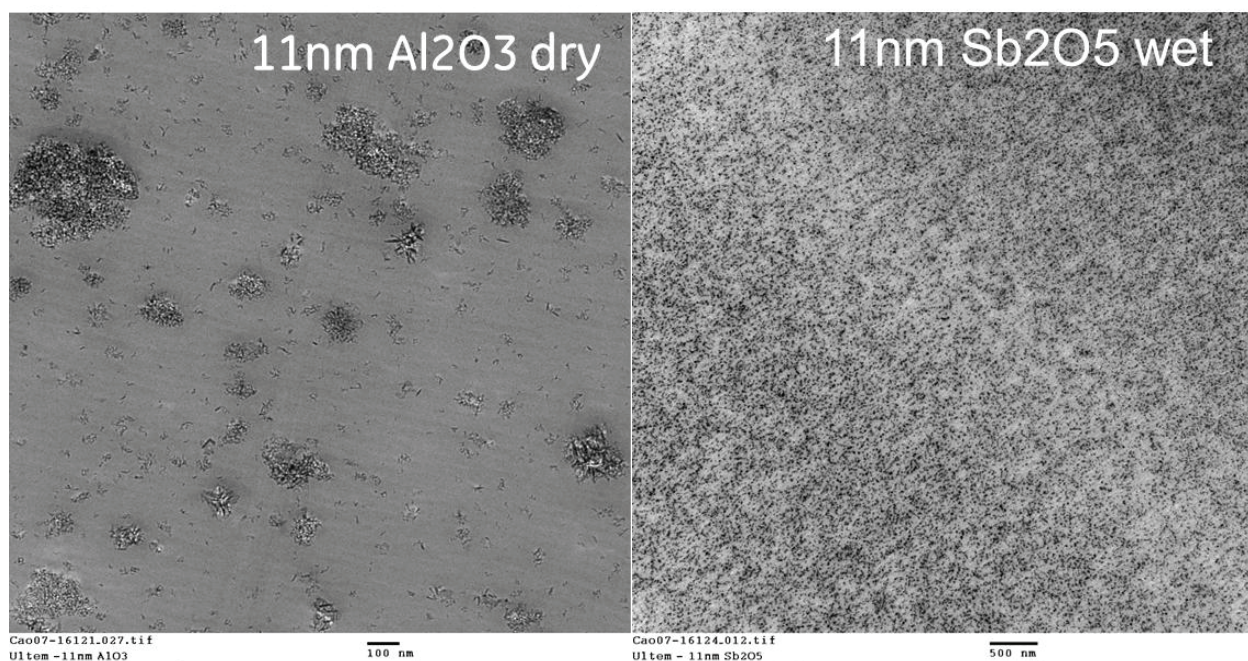


Fig. 7. Transmission electron microscope images of dry and wet nanoparticles in Ultem™ (Tan et al 2008).

### 2.3.1 Breakdown strength maintenance

In order to leverage the synergy of ceramic fillers and polymer matrices, the composite material physics should be better understood. Tan et al investigated the nano-filled polyetherimide films and emphasized the critical role of interface for the dielectric phenomenon (Tan et al 2007). In this study, Tan reported that ceramic fillers of higher breakdown strength do not impart the composite more endurance to high electrical field. Figure 8 depicts the dependence of intrinsic breakdown strength of various dielectric materials on their energy band gap. A linear increase with increasing band gap is well established. Yet data previously presented suggests that such a linear relationship cannot be correspondingly translated into nanofilled composites. A plausible explanation is that poor



particle dispersion, agglomeration, voids or defects occurring at the particle-polymer interface might over shadow the positive effect of the nanoparticles.

Tan proposed a interfacial transition model as shown in Figure 9. The dielectric permittivity is increasing from polymer matrix to fillers through a complicated interfacial region. Even inside the interfacial region, the dielectric permittivity could include a free volume (void) layer and transition layer (surface state). In these low dielectric permittivity zones, field stress are higher and could trigger localized discharge causing free carrier movement. If a good dispersion and interface are established, this type of local failure might not happen. According to Qi et al (Qi et al 2004), the critical field ( $E_b$ ) depends on the dielectric permittivity ( $\epsilon$ ), thermal conductivity ( $\kappa$ ) of the dielectric with thickness ( $d$ ):  $E_b \sim \ln(4\epsilon\kappa/\sigma_0 d^2)$ . Higher dielectric permittivity and thermal conductivity associated with ceramic fillers help extend breakdown resistance. If localized heating occurs, it can be either dissipated in oxide fillers or more quickly transported through the samples due to shortened time permittivity ( $d^2/4\kappa$ ). The thermal excitation of charges is thus restricted and breakdown strength is increased. It can be conjectured that better ceramic particle dispersion and elimination of interfacial defects could even improve the breakdown strength beyond that of the polymers. Improvments in particle processing, stabilization and dipersion control are required to realize this goal.

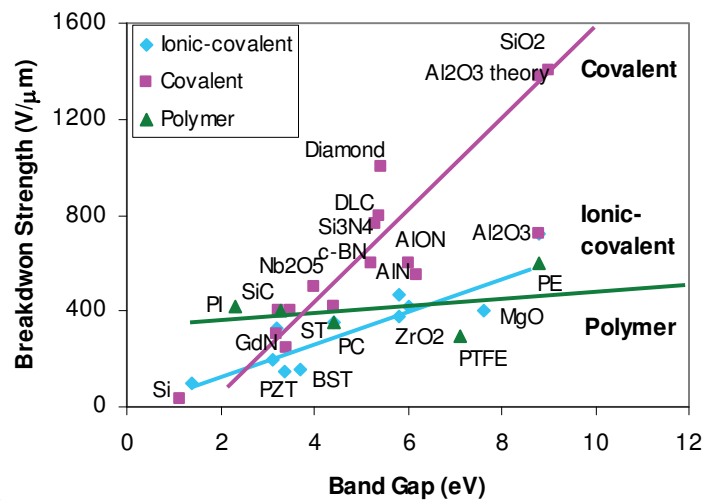


Fig. 8. Band gap dependence of breakdon strength of various dielectric materials (Tan et al 2007).

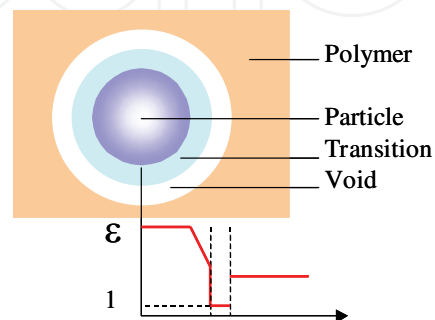


Fig. 9. A chematic model of the transition interface for a dielectric inclusion in a polymer (Tan et al 2007).

### 2.3.2 Dielectric permittivity augmentation

The increase in dielectric permittivity of polymer through addition of inorganic fillers is also challenging. For a 0-3 composite consisting of high permittivity ceramic and polymer, the logarithmic rule is most closely obeyed.

$$\log \varepsilon'_{\text{composite}} = \log \varepsilon'_{\text{matrix}} + \phi_{\text{filler}} \log \left( \frac{\varepsilon'_{\text{filler}}}{\varepsilon'_{\text{matrix}}} \right) \quad (1)$$

The volume fraction ( $\phi$ ) of fillers randomly distributed in the composite cannot exceed the value for percolation point to avoid low mechanical strength and dielectric strength. Therefore, the permittivity of the composites ( $\varepsilon'_{\text{composite}}$ ) is limited by the polymer permittivity ( $\varepsilon'_{\text{matrix}}$ ). Filling a polymer matrix with high permittivity particles was known to result in a limited increase in permittivity of the resulting composite. For example, a ferroelectric type of ceramic materials having a dielectric permittivity of several hundred at room temperature is shown in Figure 10. A significantly high dielectric permittivity peak was dramatically suppressed when added to a polymer (polyetherimide). How to synergize filler and polymer, still remains a question.

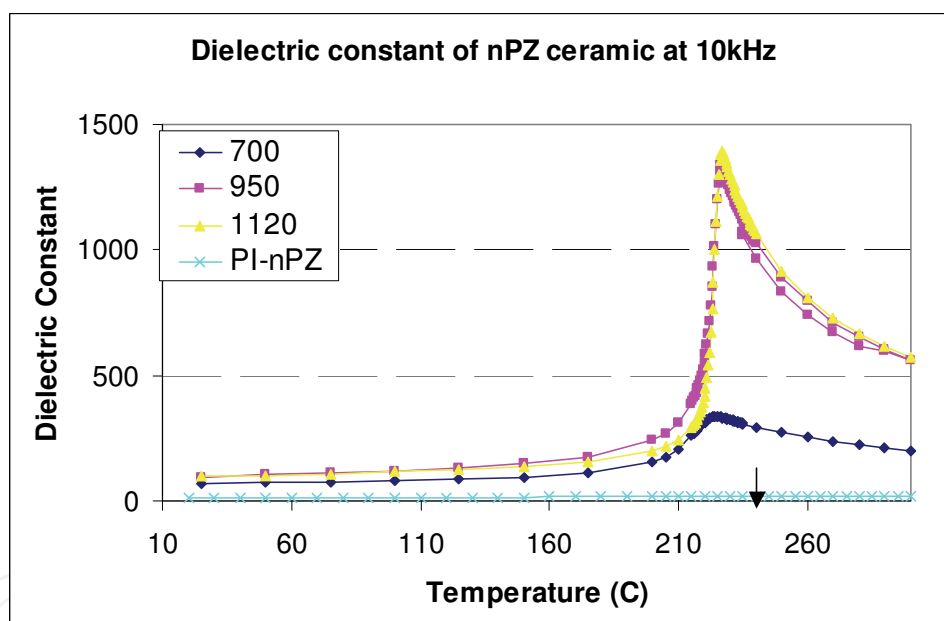


Fig. 10. The temperature dependence of the dielectric permittivity of lead zirconate ceramics and particle filled polyetherimide polymer (Tan 2010).

GE found that the higher permittivity base polymer is favored for achieving higher permittivity in nanodielectric composites. Figure 11 shows the pronounced effect in the engineering the dissimilar dielectrics. When dealing with fillers with various the shape, surface chemistry, dispersion, polarity, it still requires ingenuous thought and understanding of the physical properties of the materials. Figure 12 shows a number of materials with a wide range of dielectric permittivity and dielectric loss. Some of them are good candidates not only for their dielectric properties but also for their processing capability. With properly selected polymer matrices and inorganic fillers, one can expect to achieve good overall properties.

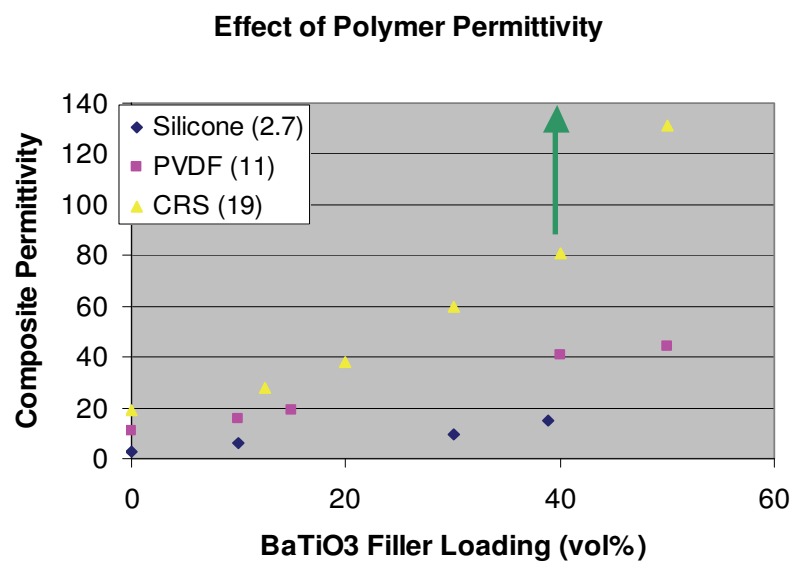


Fig. 11. The effect of the polymer matrix on the composite permittivity augmentation (Tan et al 2010).

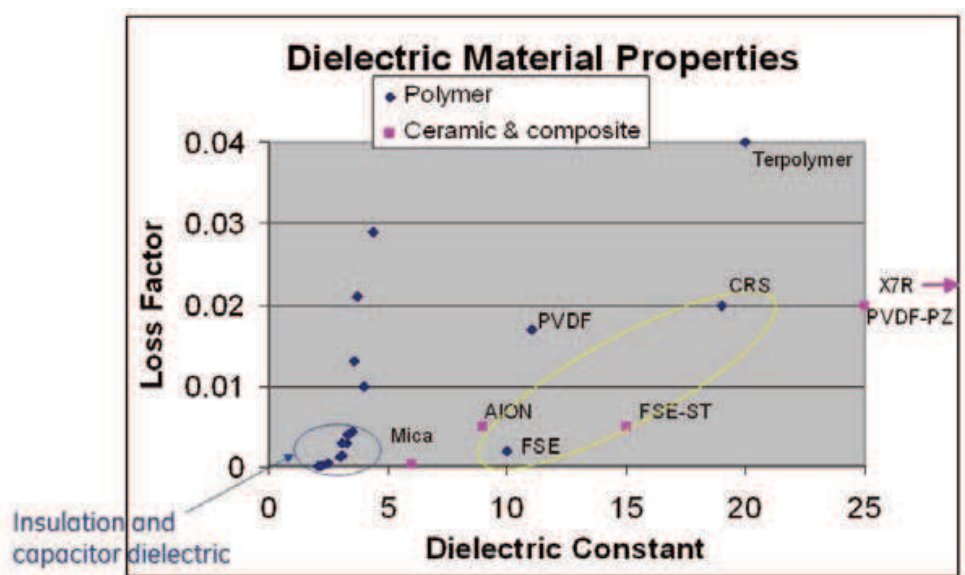


Fig. 12. Dielectric properties of various dielectric materials. High dielectric permittivity generally exhibits high dielectric loss (Tan et al 2010).

2.3.3 Nanofiller considerations

The simplest 2-phase system is a nanosphere filled polymer composite, which has received extensive investigation. A common phenomenon of such kind of composites is represented by Figure 13, where particles are of 20-100nm in diameter. It is not surprising that semiconductive and partially oxidized aluminum fillers lead to lower breakdown strength. However, for the insulative fillers with a breakdown strength of greater than 200kV/mm, the composite breakdown strength does not show much difference. It appears to slightly increase and saturate in the range of 500-600kV/mm for all insulating particles. It is

interesting to see that ceramic particles of higher breakdown strength do not impart the composites more endurance to high electrical field.

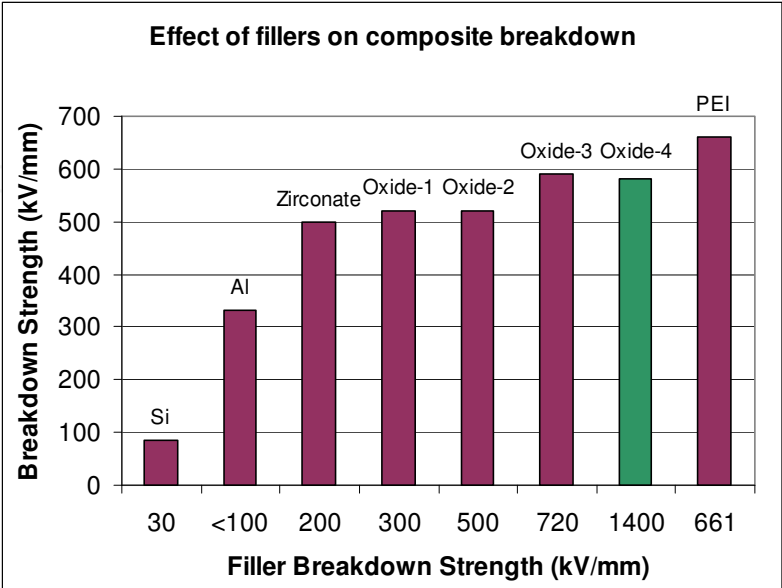


Fig. 13. The breakdown strength (BDS) of PEI composites increases with increasing BDS of 5 wt% various particles (Tan et al 2007).

When particles are smaller than 10nm, the interfacial fraction becomes dominant, which might result in interesting physical phenomena. Figure 18 depicts the increasing role of particle interface with decreasing the particle sizes (Raetzke et al 2006). With a 5 vol% particle added in a polymer, the 10nm particles will result in 40 vol% interfaces. The 5nm particles result in 95 vol% interface of the composites. When the fillers are spheroid, more complicated filler-matrix interaction and physical properties are to be expected, which requires more investigations.

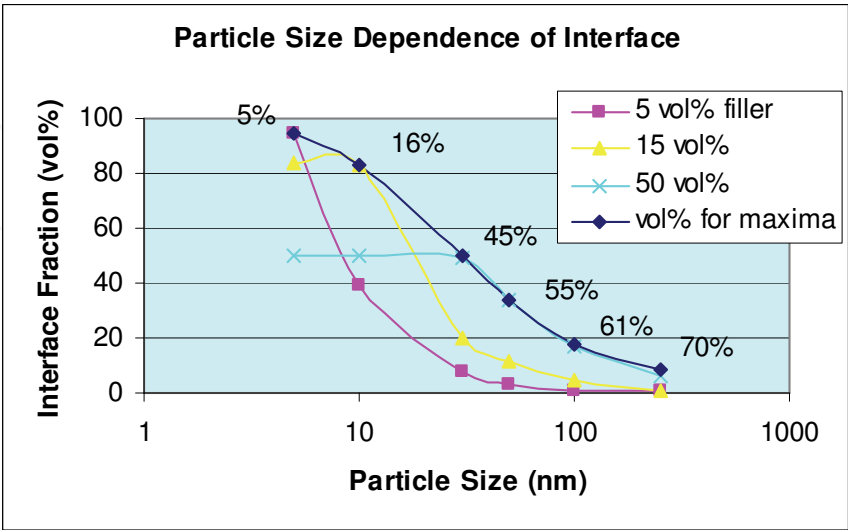


Fig. 14. The particle size dependence of the particle interfacial contribution at various loading concentration (Tan et al 2008).



2.3.4 Energy density accomplishment

In order to increase the dielectric constant of the composites, researchers mostly are interested in high permittivity nonlinear fillers like BaTiO<sub>3</sub> and TiO<sub>2</sub>. Because of the difficulty in synthesizing very fine and clean particles, researchers have added high concentration of particles. Table 2 summarized the accomplishment of several representative researches. The maximum energy density from the nanodielectric engineering so far is 15 J/cc. Recently, very fine TiO<sub>2</sub> nanoparticles were synthesized using self-assembling method (Tuncer et al 2009). The breakdown strength of the composites was increased by >20%. Therefore, better results could be achieved after optimizing nanoparticle size, surface chemistry and processing method of composites.

For polar fillers that have high permittivity, one needs to consider their polar interaction with the matrix. The alignment of dipoles in the long-range order is known to give high permittivity due to collective response to the electric field such as those in ferroelectric materials (Figure 15). Correspondingly, it also results in lower breakdown strength. For example, dipolar ordering in PVDF polymer is relatively interrupted due to randomness in molecular chain configuration as opposed to those in ferroelectric ceramics. This is why PVDF ferroelectric polymer intrinsically has lower dielectric permittivity (11) but higher breakdown strength (>400kV/mm). Similarly, controlling dipolar ordering within short-range in nanodielectrics could result in both higher permittivity and breakdown strength. A balanced value in the two parameters would be eventually beneficial to the achievement in a high energy density. Such a complex dielectric system requires not only experimental verification, but also computer modeling and simulation for conceptual guidance.

Researcher	Polymer	Filler	Process	Energy Density (J/cm <sup>3</sup> )
PennState	PVDF-CTFE PVDF-TrFE	-BaTiO <sub>3</sub> -PMNPT	Mixing	7 15
Georgia Tech	PVDF-HFP	Treated BaTiO <sub>3</sub>	Mixing	6
Northwestern Univ.	PP	BaTiO <sub>3</sub>	In-situ polymerization	9
GE	CR	Clean BaTiO <sub>3</sub>	Mixing	15

Table 2. Status of energy density in nanodielectric composite investigation

2.4 Nanodielectric composite modeling

Due to the complexity of the composite microstructures, computational methods are usually required for study of the realistic multi-component microstructures (Ang et al 2003, Tuncer

2005, Todd et al 2005, Zhou et al 2008). Boundary integral technique (Azimi et al 1994, Cheng et al 1997) and finite element method (Ang et al 2003, Zhou et al 2008) are the commonly used computational methods, which numerically solve for interface charge density distribution and spatial potential distribution, respectively, in composite systems.

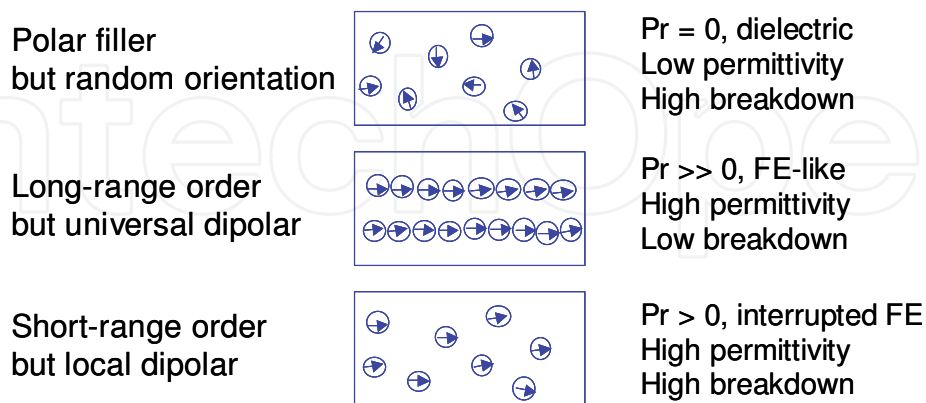


Fig. 15. Dipolar ordering model for nanofilled polymer composites (Tan et al 2007).

To avoid the complication associated with them, phase field method is recently employed to perform computational studies of composite materials (Zhang et al 2007, Wang 2010). It calculates heterogeneous distributions of polarization, charge density, local electric field, and effective dielectric permittivity of the composites, where inter-phase boundary conditions are automatically satisfied without explicitly tracking inter-phase interfaces. The phase field model of dielectric composites<sup>9</sup> is formulated in terms of polarization vector field  $\mathbf{P}(\mathbf{r})$ . The total system free energy  $F$  of a dielectric composite under externally applied electric field  $\mathbf{E}^{\text{ex}}$  is:

$$F = \int \frac{P^2(\mathbf{r})}{2\varepsilon_0\chi(\mathbf{r})} d^3r - \int \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}^{\text{ex}} d^3r + \int \frac{d^3k}{(2\pi)^3} \frac{|\mathbf{n} \cdot \tilde{\mathbf{P}}(\mathbf{k})|^2}{2\varepsilon_0}, \quad (2)$$

where  $\varepsilon_0$  is the permittivity of free space,  $\chi(\mathbf{r})$  is the spatial position-dependent dielectric susceptibility that describes arbitrary multi-component composite microstructure,  $\tilde{\mathbf{P}}(\mathbf{k})$  is the Fourier transform of the field  $\mathbf{P}(\mathbf{r})$ , and  $\mathbf{n}=\mathbf{k}/k$  is a unit directional vector in  $\mathbf{k}$ -space. The integrand of the first energy term in Eq. (2), i.e.,  $f(\mathbf{P})=P^2/(2\varepsilon_0\chi)$ , is the non-equilibrium local bulk free energy density function that defines the thermodynamic properties of linear isotropic dielectrics.

The effective susceptibility tensor  $\chi^{\text{eff}}$  of the composite is determined according to the anisotropic constitutive relation:

$$\langle P_i \rangle = \varepsilon_0 \chi_{ij}^{\text{eff}} \langle E_j \rangle, \quad (3)$$

where  $\langle \mathbf{E} \rangle = \mathbf{E}^{\text{ex}}$ . The effective anisotropic dielectric permittivity tensor is:

$$k_{ij}^{\text{eff}} = \delta_{ij} + \chi_{ij}^{\text{eff}}, \quad (4)$$

where  $\delta_{ij}$  is Kronecker delta.

Wang et al (2011) did a series of computation for a composite containing well-dispersed particles of 20% volume fraction arranged into square or quasi-hexagonal lattices. The particle interactions are assumed not strong enough to significantly reduce the depolarization effect of individual particles, and the composites exhibit moderate effective susceptibility in all directions. However, with particles aligned into chains, particles strongly interact through electrostatic forces in the chain direction to effectively reduce the depolarization effect of the particles in each chain, resulting in significantly improved composite susceptibility along the chain direction as shown in Figure 16. In the transverse direction, on the other hand, the strong chain-chain interactions enhance the depolarization effect, leading to decreased composite susceptibility in direction perpendicular to the chains. Therefore, the composites exhibit significant susceptibility anisotropy, which results from the microstructure anisotropy of the filler particle arrangement. In fact, alignment of filler particles into chains establishes pseudo-1-3 connectivity as compared to 0-3 connectivity of dispersed particles (Newnham 1978), which forms continuous paths of high-susceptibility phase and enhances filler particle polarization under external electric field applied along the chain direction.

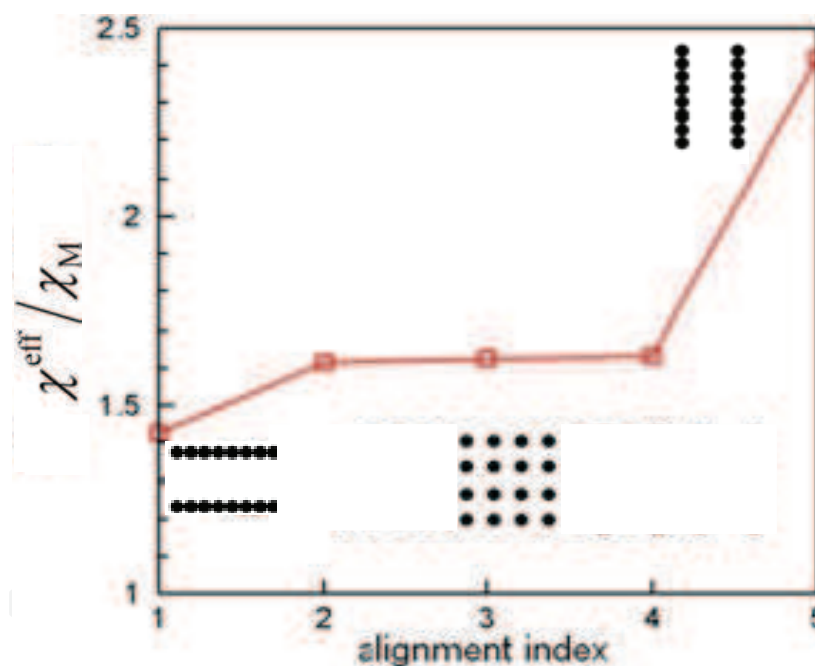


Fig. 16. Effect of filler particle microstructural arrangement on effective composite susceptibility in composites composed of 20% volume fraction of circular fillers with dielectric susceptibility  $\chi_F/\chi_M = 10$ . Insets illustrate the corresponding particle arrangements. Arrow indicates electric field (i.e.,  $E$ ) direction.  $\chi^{eff}$  is the susceptibility component in  $E$  direction (Wang et al 2011).

Because of the issues associated with high volume fraction such as poor filler dispersion, porosity and defected filler-matrix interfaces, an appropriate range of filler volume fraction should be designed. To investigate the effect of filler particle volume fraction on the effective dielectric permittivity of composites, composites composed of different volume fractions of same-sized circular fillers with the same dielectric susceptibility  $\chi_F/\chi_M = 10$  are considered.

In particular, the upper and lower bounds for  $\chi^{\text{eff}}$  are obtained with parallel and series two-phase morphologies, respectively, and are given as

$$\chi_{\text{upper}}^{\text{eff}} = V\chi_F + (1-V)\chi_M, \quad \frac{1}{\chi_{\text{lower}}^{\text{eff}}} = \frac{V}{\chi_F} + \frac{1-V}{\chi_M}, \quad (5)$$

where  $V$  is filler phase volume fraction. It is found that at low volume fraction (e.g.,  $V < 30\%$ )  $\chi^{\text{eff}}$  is closer to the lower bound  $\chi_{\text{lower}}^{\text{eff}}$ , while at high volume fraction (e.g.,  $V > 60\%$ )  $\chi^{\text{eff}}$  starts departing from  $\chi_{\text{lower}}^{\text{eff}}$  to approach the upper bound  $\chi_{\text{upper}}^{\text{eff}}$ . This transition behavior of  $\chi^{\text{eff}}$  at low and high filler volume fraction with respect to  $\chi_{\text{lower}}^{\text{eff}}$  and  $\chi_{\text{upper}}^{\text{eff}}$  is associated with the increasingly strong particle interactions and gradual establishment of particle connectivity when filler volume fraction increases. Figure 17 presents the computational results for dispersed fillers, the aligned filler chains in parallel and in perpendicular to electric field direction, respectively. It can be found that the alignment of particles into chains is an effective way to establish filler connectivity in volume fraction range much lower than that required by randomly dispersed fillers. This may help alleviate the problems encountered during composite fabrication with high filler volume fractions.

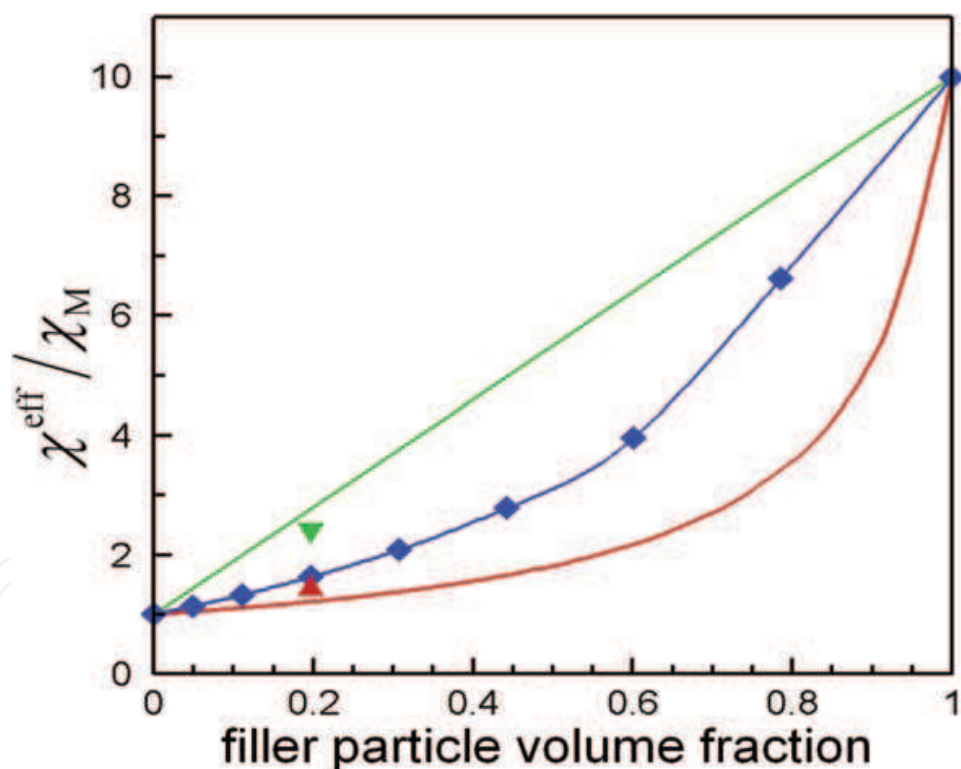


Fig. 17. Effect of filler particle volume fraction on effective composite susceptibility in composites composed of fillers with dielectric susceptibility  $\chi_F/\chi_M = 10$ . Green and red curves represent upper and lower bounds based on rule of mixtures for parallel and series two-phase morphologies, respectively. Blue curve represents computational results for composites composed of same-sized dispersed circular fillers. Green and red triangles ( $\uparrow$ ,  $\downarrow$ ) correspond to composites with filler particles aligned into chains parallel and perpendicular to electric field direction, respectively, as shown in Fig. 16 (Wang et al 2011).



### 3. Conclusion and future interests

Synthesis of higher permittivity composites by mixing the various fillers (ceramic, semiconductor, metallic, organic) has been conducted over the last decade. Engineering the existing materials requires advances in designing, processing, forming and manufacturing technologies. Successes require (i) higher dielectric permittivity polymers, (ii) higher dielectric permittivity ceramics, (iii) proper dispersion, and (iv) good interfacial adhesion between filler and polymer. Fillers that have been studied include ceramics ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_2$ , PZT, PMN-PT, PLZT,  $\text{MgO}$ , Mica, layered silicate,  $\text{Si}_3\text{N}_4$ , BN), semiconductors (Si, SiC, ZnO, varistor particles,  $\text{SnO}_2$ , antimony modified  $\text{SnO}_2$ ), metals (Al, Cu, Ag, Co-ACAC, Pt), carbon (black, CNTs). Great deal of knowledge has been acquired about nanodielectrics, however, there is still no breakthrough in increasing dielectric strength and permittivity simultaneously. In order to enhance dielectric properties, mechanical flexibility and thermal stability, further investigations are required, which can include the following subjects.

- What types of ceramic fillers and polymers are able to synergize the dielectric properties?
- What type of fillers, their size, shape and orientation are the best choice for composites?
- What kinds of filler surface chemistry promote filler dispersion and better properties?
- How does filler interface contribute to dielectric properties?
- How effective are the insulation coated nanofillers on dielectric property augmentation?
- What needs to be done to develop the polymers having high dielectric permittivity, high temperature and also low dielectric loss?
- How does the nanodielectric engineering improve both dielectric properties and thermal conduction properties?

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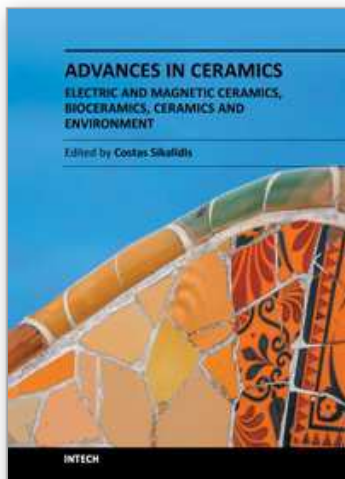
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